phines, arsines, 2,2′-bipyridine, etc.) were used in conjunction with SCN^-, π bonding was not the single major factor controlling the type of metal–thiocyanate linkage. Moreover, the effects of π interaction on Pd–CNS bonding in the complexes $PdL_2(CNS)_2$ are expected to be small due to the *trans* positions of the two thiocyanates and the two ligands L. As a result, minor changes in various electronic and steric properties of the ligands employed frequently produce striking effects on the mode of palladium–thiocyanate attachment.

It is surprising that the $RhL_2(CO)(NCS)$ complexes containing tertiary phosphines and triphenylstibine retain their integrity in solution whereas the analogous arsine derivatives undergo partial dissociation with the resultant formation of the dinuclear $Rh_2L_2(CO)_2(CNS)_2$. The extent of dissociation among the arsine complexes increases with L in the order $As(C_6H_5)_3 < As(p\text{-}ClC_6H_4)_3 < As(m\text{-}CF_3C_6H_4)_3$ and thus parallels the increasing π-bonding ability of L (and presumably also decreasing σ bonding), reflected in the values of the CO stretching frequencies.

However, an examination of the carbonyl stretching frequencies of $Rh(MR_3)_2(CO)(NCS)$ (M = P, As, and Sb) reveals that for a given R the extent of Rh–CO π bonding decreases as M changes from antimony to arsenic and to phosphorus. This then indicates that in rhodium(I) complexes the phosphines π bond somewhat better than the arsines and stibines. In the light of these data the ability of $RhL_2(CO)(NCS)$ to undergo loss of the ligand L cannot be ascribed solely to the lability of the Rh–L π bond brought about by a strong π interaction in the *trans*-RhL_2 moiety, but must reflect also a relatively weak Rh–L σ bond.

Acknowledgment.—The support of this investigation by the National Science Foundation is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, NORTH CAROLINA 27514

Low-Frequency Infrared Spectral Studies on Copper(II) Halide Complexes with Substituted Pyridine N-Oxides[1,2]

BY ROBIN WHYMAN AND WILLIAM E. HATFIELD

Received May 22, 1967

The far-infrared spectra of substituted pyridine N-oxide complexes with copper(II) halides of empirical formula $CuX_2 \cdot L$ and $CuX_2 \cdot 2L$, where X = Cl or Br, have been measured and infrared-active metal–chlorine stretching modes of vibration assigned. The former compounds, which all display subnormal magnetic moments and presumably possess binuclear oxygen-bridged structures, afford terminal metal–chlorine stretching frequencies in the range 342–305 cm^{-1}. The 2:1 chloride complexes may be divided into two types based on their colors and on the position of the metal–chlorine vibrational modes. The first class contains the green compounds and these exhibit metal–chlorine stretching modes at higher frequencies than the corresponding 1:1 complexes. In contrast, the two members of the second class, which are yellow in color, absorb at lower frequencies. These results are compared with the corresponding substituted quinoline N-oxide systems and differences and trends are discussed. Metal–oxygen stretching frequencies are tentatively assigned for the 2:1 derivatives and magnetic susceptibilities at 302, 196, and 77°K are included for several complexes.

Introduction

Recently, we reported the assignment of infrared-active metal–chlorine stretching vibrations for a series of substituted quinoline N-oxide complexes with copper(II) chloride.[3] The use of these frequencies as a criterion of oxygen- or halogen-bridged structural species was proposed. Thus the 1:1 complexes which exhibited subnormal magnetic moments and, by analogy with the parent pyridine N-oxide–copper(II) chloride complex,[4] posssess binuclear oxygen-bridged structures, afforded "terminal" metal–chlorine stretching frequencies in the range 344–325 cm^{-1}. For the condensed compounds which showed normal magnetic behavior the maxima were shifted *ca.* 40 cm^{-1} to lower energy, occurring in the range 308–280 cm^{-1}. This shift was considered to reflect the difference between structural species containing terminal and bridging metal–chlorine bonds. The 2:1 derivatives, which also displayed normal, temperature-independent magnetic moments, afforded maxima in the lower range.

As an extension to this work, the far-infrared spectra of a series of substituted pyridine N-oxide complexes with copper(II) halides have been measured and interpreted, and the results are reported herein. Additionally, magnetic susceptibilities at 302, 196, and 77°K are reported.

---

[1] This paper is part V of both the series "Spin–Spin Coupling in Binuclear Complexes" and "Substituted Heterocyclic N-Oxide Complexes."

[2] This material was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[3] W. E. Hatfield, D. B. Copley, and R. Whyman, *Inorg. Nucl. Chem. Letters*, **2**, 373 (1966); R. Whyman, D. B. Copley, and W. E. Hatfield, *J. Am. Chem. Soc.*, **89**, 3135 (1967).

[4] H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

TABLE I

ANALYTICAL DATA

Ligand	Halide	Ligand: salt ratio	Analyses, %							
			C		H		N		Cu	
			Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
4-Methoxypyridine N-oxide	$CuCl_2$	1:1	27.76	27.73	2.80	2.70	5.39	5.39	24.25	24.47
	$CuCl_2$	2:1	37.74	37.44	3.87	3.64	7.17	7.28	16.36	16.52
	$CuBr_2$	1:1	20.88	20.65	2.10	2.01	4.20	4.02	18.20	18.23
	$CuBr_2$	2:1	30.61	30.40	2.94	2.96	6.19	5.91	13.99	13.42
3-Picoline N-oxide	$CuBr_2$	2:1	32.72	32.62	3.22	3.17	6.20	6.34	14.39	14.40
2-Picoline N-oxide	$CuBr_2$	1:1	21.90	21.66	2.22	2.11	3.94	4.21	19.04	19.12
4-Nitropyridine N-oxide	$CuCl_2$	1:1	21.99	21.85	1.66	1.46	10.05	10.20	23.09	23.14

Experimental Section

Preparation of the Substituted Pyridine N-Oxides.—4-Nitro and 4-chloropyridine N-oxides, 3- and 4-picoline N-oxides, and 2,6-lutidine N-oxide were prepared by the method of Ochiai.[5] The melting points of these ligands were consistent with reported values. Pyridine N-oxide, 4-methoxypyridine N-oxide, 2-picoline N-oxide, and 2,4,6-collidine N-oxide were obtained commercially.

Preparation of the Complexes. Method A.—In general the 1:1 complexes were prepared by the addition of a solution of the substituted pyridine N-oxide in ethanol to a stoichiometric amount of an ethanolic solution of $CuCl_2 \cdot 2H_2O$ or $CuBr_2$. The products either crystallized immediately or upon standing for a short time and were filtered, washed with a small quantity of ethanol, and dried in the air.

Method B.—The 2:1 complexes were generally prepared by the slow addition of a warm solution of the copper halide in 1-butanol to an excess of a hot solution of the ligand in 1-butanol. For the chlorides the green mixture was heated at 70° for 30 min and then allowed to cool. On standing overnight green or yellow crystals of the 2:1 complex precipitated. These were filtered, washed with 1-butanol, and dried in the air.

Analytical Data.—Microanalyses for carbon, hydrogen, and nitrogen were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Copper analyses were determined by EDTA titration using Snazox as indicator.[6] Analytical data for the new complexes are presented in Table I. Satisfactory copper analyses were obtained for those compounds which have been reported previously.

Magnetic Susceptibility Determinations.—Magnetic susceptibilities were determined as a function of temperature by the Faraday method using equipment and procedures which have been described previously.[7] Mercury tetrathiocyanatocobaltate-(II) was used as magnetic susceptibility standard, and diamagnetic corrections were estimated from Pascal's constants.[8]

Spectral Measurements.—Infrared spectra in the range 1300–250 cm^{-1} were recorded with a Perkin-Elmer Model 521 grating spectrophotometer. The samples were measured as Nujol mulls supported between cesium bromide plates.

Results and Discussion

Magnetic Data.—For the seven new and four recently characterized complexes magnetic susceptibilities were determined at 302, 196, and 77°K only, since these measurements were sufficient to distinguish between different types of magnetic behavior. The molar magnetic susceptibilities were calculated on the basis of a formula weight per copper(II) ion in all cases and magnetic moments were obtained from the expression $\mu_{eff} = 2.84(\chi_m^{cor}T)^{1/2}$. The magnetic data are summarized in Table II.

TABLE II

MAGNETIC DATA

Complex	μ_{eff}, BM per Cu(II) ion 302°	196°	77°
4-Methoxypyridine N-oxide			
$CuCl_2 \cdot L$	0.51	0.41	0.34
$CuCl_2 \cdot 2L$	1.95	1.93	1.87
$CuBr_2 \cdot L$	0.59	0.46	0.40
$CuBr_2 \cdot 2L$	2.02	2.03	1.96
4-Picoline N-oxide			
$CuCl_2 \cdot 2L$	1.96	1.93	1.89
3-Picoline N-oxide			
$CuCl_2 \cdot 2L$	1.97	1.93	1.86
$CuBr_2 \cdot 2L$	1.69	1.49	0.63
2-Picoline N-oxide			
$(CuCl_2)_3L_2 \cdot 2H_2O$	1.22	1.17	1.13
$CuCl_2 \cdot 2L$	2.00	1.97	1.91
$CuBr_2 \cdot L$	0.51	0.44	0.28
4-Nitropyridine N-oxide			
$CuCl_2 \cdot L$	1.01	0.64	0.33

The four 1:1 complexes display subnormal magnetic moments which decrease with decreasing temperature. The observed antiferromagnetism is similar to that noted in the parent compound of the series, pyridine N-oxide–copper(II) chloride, and the presence of analogous binuclear oxygen-bridged structural units may be inferred.

A comparison of the room-temperature magnetic moments of the copper chloride complexes with those of 4-methoxy- and 4-nitropyridine N-oxide shows that the magnetic susceptibility of the former is considerably lower. This behavior may be predicted on the basis of electronic effects of the substituents. The increased donor strength of 4-methoxypyridine N-oxide relative to the 4-nitro derivative is reflected in an increase in the electron density in the orbitals of the bridging oxygen atoms. Thus the exchange interaction between unpaired electrons on the copper ions is enhanced, and, consequently, the magnetic moment of the 4-methoxypyridine N-oxide complex is substantially lower.

With one exception, the 2:1 complexes display normal magnetic moments, *i.e.*, values greater than or equal to 1.73 BM per copper(II) ion, which are essentially independent of temperature and characteristic of magnetically dilute species. The 3-picoline N-oxide compound with copper bromide shows a room-temperature magnetic moment of 1.69 BM which decreases to 0.63 BM at 77°K. Similar behavior is found with the corresponding 4-picoline N-oxide complex,[9] although for

---

(5) E. Ochiai, *J. Org. Chem.*, **18**, 548 (1953).

(6) G. Guerrin, M. V. Sheldon, and C. N. Reilley, *Chemist-Analyst*, **49**, 36 (1960).

(7) W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, **5**, 1855 (1966).

(8) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960.

(9) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

TABLE III

SUMMARY OF METAL–CHLORINE STRETCHING FREQUENCIES (cm^{-1}) FOR 1:1 AND 2:1 COMPLEXES[a]

Ligand	$CuCl_2 \cdot L$			$CuCl_2 \cdot 2L$			Color of 2:1 complex
4-Methoxypyridine N-oxide	324 vs			327 s			Green
4-Picoline N-oxide	327 s	312 s		339 vs	316 m	296 m	Green
Pyridine N-oxide	330 w, sh	311 vs			310 vs	286 vs	Yellow-green
4-Chloropyridine N-oxide	317 s			341 s			Green
4-Nitropyridine N-oxide	305 vs			345 s			Green
3-Picoline N-oxide	316 vs			322 vs			Green
2-Picoline N-oxide	315 m, sh	302 s	291 s[b]	328 vs			Green
2,6-Lutidine N-oxide	342 vs	326 vs			319 s	297 vs	Yellow
2,4,6-Collidine N-oxide	337 vs				318 s	330 m, sh	Yellow

[a] w = weak, m = medium, and s = strong intensity; v = very and sh = shoulder. [b] Empirical formula $(CuCl_2)_3L_2 \cdot 2H_2O$.

both these ligands the respective copper chloride derivatives are magnetically normal. These two copper bromide salts and the pyridine N-oxide–copper chloride complex are the only examples of 2:1 compounds reported to exhibit subnormal magnetic moments. The structures of the former are probably similar to that which has been established for the copper chloride complex,[10] *i.e.*, the basic binuclear oxygen-bridged unit with a second N-oxide ligand attached to each copper atom.

During the course of this work, magnetic susceptibility data for the copper(II) chloride complexes with 2- and 4-picoline N-oxides were reported elsewhere[11] and the results obtained in our investigation are consistent.

Far-Infrared Spectra.—Infrared spectra were measured as Nujol mulls in the range 1300–250 cm^{-1}, and the observed bands in the low-frequency region (550–250 cm^{-1}), together with maxima which have been assigned as nitrogen–oxygen stretching modes of vibration, have been deposited with the American Documentation Institute.[12] For several of the complexes the nitrogen–oxygen stretching frequencies have been assigned previously and our results are essentially consistent with the earlier work.[9,13]

Previous far-infrared spectral studies on complexes containing metal–halogen bonds indicate that metal–chlorine stretching frequencies occur in the range 250–350 cm^{-1} and metal–bromine frequencies from below 200–250 cm^{-1}.[14] Comparison of the spectra of the copper chloride complexes with those of the bromides and the free ligands facilitated the assignment of the infrared-active copper–chlorine stretching frequencies. Although maxima were observed with some ligands in the 250–350-cm^{-1} region, the bands which have been assigned to metal–chlorine vibrational modes are generally considerably more intense. Those peaks which are assigned as metal–chlorine stretching frequencies are summarized in Table III.

Assuming the presence of similar structural species and the relationship $\nu(M\text{–}Br)/\nu(M\text{–}Cl) = 0.75$,[14] a metal–chlorine stretching frequency of 320 cm^{-1} would correspond with a metal–halogen absorption at *ca.* 240 cm^{-1} in the corresponding bromide complex. Frequencies of this order lie just outside the range of the instrument, the lower limit of which occurs at *ca.* 245 cm^{-1}. Spectra of the bromides frequently showed increasing absorption in the region 280–250 cm^{-1} but generally no clearly defined maxima could be distinguished.

The condensed complexes all display subnormal magnetic moments and, with one exception, the presence of binuclear oxygen-bridged structures is presumed. Thus the frequencies presented in Table III for the compounds with a ligand:salt ratio of 1 represent the vibrations of terminal metal–chlorine bonds. The range of frequencies (342–305 cm^{-1}) is considerably wider than that found for the substituted quinoline N-oxide complexes displaying subnormal magnetic moments. However, in the latter case, only ligands of relatively high pK_a values form the oxygen-bridged species, whereas for the pyridine N-oxides discussed here all of the ligands afford this type of complex. Since we are dealing with a considerably wider range of pK_a values (and hence donor properties), we may anticipate a greater variation in the position of the frequencies.

For the polymeric 2-picoline N-oxide compound, of empirical formula $(CuCl_2)_3L_2 \cdot 2H_2O$, the values of the copper–chlorine stretching frequencies are very similar to those observed in the substituted quinoline N-oxide complexes of similar stoichiometry. Thus the spectrum of the 4-chloroquinoline N-oxide derivative exhibits maxima at 308 s and 290 s cm^{-1} which were assigned to these modes of vibration.[3] This implies the presence of similar structural entities, of which one possibility is analogous to that reported by Willett and Rundle for $Cu_3Cl_6 \cdot 2CH_3CN$.[15] This supports the earlier conclusion based on magnetic data.[11]

As noted previously, the 2:1 copper chloride complexes, with one exception, show normal magnetic moments which are independent of temperature. The pyridine N-oxide complex has been shown to contain

---

(10) J. C. Morrow, private communication.

(11) M. R. Kidd, R. S. Sager, and W. H. Watson, *Inorg. Chem.*, **6**, 946 (1967).

(12) Material supplementary to this article has been deposited as Document No. 9548 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is rquired. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(13) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961); S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963); Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Japan*, **39**, 58 (1966).

(14) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

(15) R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).

the basic binuclear oxygen-bridged unit, and, as a result, the metal–chlorine stretching frequencies exhibited by this compound cannot be included for the purposes of comparison.

The remaining complexes fall into two classes as indicated by their colors. The green compounds exhibit metal–chlorine stretching frequencies at slightly higher values than the 1:1 complexes whereas the yellow isomers absorb at lower frequencies. This is the reverse of the situation found with the nitrogen–oxygen modes of vibration.[12] From preliminary X-ray crystallographic investigations, Watson has shown that the green 4-picoline N-oxide complex must be *trans*-square-planar and that the green 2-picoline N-oxide complex may be *trans*-square-planar, whereas the yellow 2,6-lutidine N-oxide derivative contains a structure which is midway between square-planar and tetrahedral.[11] It may be approximated by rotating two *cis* ligands by 45° about an axis bisecting them and passing through the copper atom or by rotating two tetrahedral ligands by 45° around an axis bisecting them and passing through the copper atom.

The association of the higher metal–chlorine stretching frequencies with the green complexes is considered to reflect the presence of terminal metal–chlorine bonds, *i.e.*, structures containing chlorine atoms which do not interact with copper ions from neighboring molecules. In view of the paucity of structural data at the present time on the yellow isomers, extensive speculation of the significance of the band shifts is not warranted.

The 2:1 copper(II) chloride complexes with substituted quinoline N-oxides show frequencies of a similar order to those of the yellow isomers and the presence of polymeric halogen-bridged structures was postulated here.[3] The relatively high metal–chlorine stretching frequency of 342 cm^{-1} observed with the 3-nitro-6-methylquinoline N-oxide complex may be explained, in the light of evidence from the pyridine N-oxide series, in terms of the presence of the *trans* isomer.

In the spectrum of the 4-picoline N-oxide complex, two peaks of medium intensity are observed at 316 and 296 cm^{-1}, in addition to the main band at 339 cm^{-1}. These maxima are considerably more intense than those present in the copper bromide complexes in this region and hence are not thought to be associated solely with ligand vibrations. In view of the similarity of the position of these frequencies to those of both the yellow isomers and the 2:1 pyridine N-oxide compound, the presence of a small amount of either the yellow form or the condensed 2:1 complex is implied. The essentially temperature-independent magnetic moment of 1.96 BM favors the former, since the presence of even a small quantity of the condensed complex would be anticipated to cause a considerable reduction in the magnetic moment at 77°K.

Spectra of the 2:1 copper chloride and bromide complexes exhibit additional relatively intense absorptions in the range 350–450 cm^{-1}. These bands are not observed in the spectra of the ligands and may be tentatively assigned as infrared-active metal–oxygen stretching vibrations. They are summarized in Table IV. In support of these assignments the frequencies for the 4-substituted pyridine N-oxide complexes occur at similar, but slightly lower, energies to those observed in the series $[Cu(4\text{-}RC_5H_4NO)_4](ClO_4)_2$.[16] Also they show a similar trend in frequency change upon variation of *R*. Thus for R = CH_3 or Cl the metal–oxygen vibrational modes occur at considerably higher frequencies than with R = OCH_3 or NO_2.

TABLE IV

METAL–OXYGEN STRETCHING FREQUENCIES FOR THE 2:1 COMPLEXES

Ligand	$CuCl_2$		$CuBr_2$	
4-Methoxypyridine N-oxide		347 m, sh		330 m
4-Picoline N-oxide		426 s	417 m	408 w, sh[a]
Pyridine N-oxide		. . .[a]		367 vs
4-Chloropyridine N-oxide		420 s	Not isolated	
4-Nitropyridine N-oxide		370 m	Not isolated	
3-Picoline N-oxide		373 vs	380 s	359 m, sh[a]
2-Picoline N-oxide		380 s	Not isolated	
2,6-Lutidine N-oxide	408 m	370 s	418 m	368 m
2,4,6-Collidine N-oxide	453 m	435 m	450 m	432 m

[a] These complexes display subnormal magnetic moments.

The numerical values of the metal–oxygen stretching frequencies do not appear to correlate with any of the commonly used substituent constants for the groups attached to the pyridine ring. However, in view of the complexity of the vibrational problem, this is hardly surprising. Because of the possibility of coupling with other vibrations of similar symmetry properties, these are not pure modes of vibration and can only be considered to be "essentially" metal–oxygen stretching modes. Similar considerations apply to the metal–chlorine stretching frequencies discussed previously.

Additional absorptions in the 350–450-cm^{-1} range are also observed with several of the 1:1 complexes and these may be associated with the corresponding metal–oxygen vibrations. However, in view of the considerably different structural units present in the 1:1 and 2:1 species, it seems unlikely that the metal–oxygen stretching frequencies arising from "terminal" and "bridged" pyridine N-oxide ligands should occur at very similar energies. The bands observed in the spectra of the 1:1 derivatives are also much less intense than the maxima assigned as metal–oxygen vibrations in the 2:1 complexes.

Acknowledgments.—This work was supported by the Advanced Research Projects Agency. The authors wish to thank Dr. G. G. Long of North Carolina State University for the use of the Perkin-Elmer Model 521 grating infrared spectrophotometer.

---

(16) R. Whyman, W. E. Hatfield, and J. S. Paschal, *Inorg. Chim. Acta*, **1**, 113 (1967).